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METHOD FOR THE PREPARATION OF CELLULOSE ETHERS

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This invention relates to a method for the alkylation of cellulose, and more particularly to a method for the alkylation of cellulose in the presence of an aliphatic alcohol.

As is well known, alkyl ethers of cellulose are produced by the action of an alkylating agent, such as, an alkyl halide, on a cellulose in the presence of an alkali, such as caustic soda, in the presence of more or less water. Heretofore, the addition of alcohol to the reaction mixture has been suggested. Thus, U. S. Patent 1,188,376 suggests the alkylation of cellulose in the presence of an aqueous-alcoholic solution of caustic. The use of alcohol has in general been found to be disadvantageous in the alkylation of cellulose, since the alcohol reacts with the alkylating agents in the presence of caustic alkali, thus decreasing the amount of alkylating agent present for reaction with the cellulose. The result of the use of alcohol in the alkylation of cellulose has been incomplete alkylation in spite of very high consumption of the alkylating agent, lack of uniformity and a degraded product.

I have found that the use of alcohol in the alkylation of cellulose under different and limited conditions avoids the undesirable results usually obtained by the use of alcohol, and makes possible the etherification of cellulose in a much shorter time than used heretofore, or in the same time at a lower temperature. A further advantage is an increased yield which may be 10 to 20% higher than that obtained in the processes used heretofore.

The method in accordance with this invention calls for reacting cellulose with an alkylating agent in the presence of an aliphatic alcohol in amount within the range of about 20% to about 90% by weight of the cellulose present. I prefer to restrict the amount of alcohol to an amount within the range of about 40% to about 70% of the weight of the cellulose. The alcohol will desirably contain the same alkyl group as that contained in the alkylating agent, and will desirably be substantially anhydrous, although a moderate water content is not objectionable. Water may also be present as moisture in the cellulose. The maximum total water content of the reaction mixture will desirably be not more than 100%, and preferably not more than 30% of the weight of cellulose used. The alkylating agent used may be an alkyl halide or an alkyl sulphate and preferably an alkyl chloride. Thus, for example, the alkylating agent may be ethyl chloride, ethyl bromide, butyl chloride, butyl bromide, diethyl sulfate, etc. The amount of alkali used, preferably caustic soda, will be any quantity customarily used by the art in the alkylation of cellulose. I have found that it is usually desirable to use an amount of alkali within the range of about 5 moles to about 17 moles and preferably within the range of about 8 moles to about 14 moles for each mole of cellulose (calculated as $C_6H_{10}O_5$) present, depending upon the desired alkoxy content of the product.

In carrying out my invention I may use any type of cellulose material such as, purified wood pulp or cotton linters. The caustic used should be of high purity, altho the presence of sodium chloride is not objectionable. It is advantageous to use a caustic in granular or flaky form, altho lumps or powder may be used. The amount used will depend mainly upon the degree of etherification desired in the product, and the amount of alcohol used in the reaction mixture. Thus, for example, in the production of ethyl cellulose having 48–49% ethoxy, the molecular proportion of caustic to cellulose unit ($C_6H_{10}O_5$) is 9:1, while the amount of alcohol should be about 60% by weight of the cellulose. The amount of alkylating agent used may vary within wide limits. In preparing cellulose ethers having good solubility in organic solvents, I prefer to use a large excess of the alkylating agent. Thus, I may use 15–20 moles of alkyl chloride to each cellulose unit. The alkylating agent serves not only as a reactant but also as a medium for the reaction, and a large part of the excess may be recovered unchanged at the end of the reaction.

This excess of the alkylating agent may be replaced to a greater or lesser extent by an indifferent organic solvent, such as benzene, toluene, dioxan and the like, which acts both as diluent (medium for the reaction) and as solvent for the cellulose alkyl ether formed. However, the time required to complete the reaction in the presence of such diluents is greater at any one temperature than when an excess of the alkylating agent serves as medium for the reaction.

The alcohol used may be a lower aliphatic alcohol, such as for example, methanol, ethanol, n-propanol, isopropanol, n-butanol and so forth. To avoid the formation of an excessive number of by-products I prefer to use an alcohol containing the same alkyl group as that contained in the alkylating agent. Thus, for example, I use ethanol when ethylating cellulose with ethyl chloride.

When using an alkyl chloride as an alkylating agent, as I prefer to do, the reaction is carried out in an autoclave provided with a stirrer or con-

structed for rotating or tumbling motion to effect agitation. The ingredients of the alkylation mixture may be introduced into the autoclave simultaneously or in any order or combination. Thus, I may impregnate the cellulose with a mixture of the alcohol and the alkylating agent and then add the caustic. I have found, however, that it is desirable to secure a very uniform distribution of the alcohol in the cellulose at the beginning of the reaction. This may be conveniently attained by immersing the cellulose in a large volume of alcohol and then removing the excess by pressure.

After all of the ingredients of the alkylation mixture are in the autoclave it is heated either rapidly or gradually to reaction temperature. I find that it is advantageous to heat the mixture very gradually. A desirable reaction temperature is determined largely by the reactivity and amount of the alkylating agent present. Thus, when using ethyl chloride as an alkylating agent, a temperature within the range of about 90° C. to about 150° C. and preferably within the range of about 100° C. to about 130° C. will be found satisfactory. It will be found that the higher the temperature the more rapid the reaction, while the lower temperatures insure greater uniformity and higher viscosity of the product.

As a further illustration of the method in accordance with this invention I may cite the following examples:

Example I

Twenty-six grams purified cotton linters and 54 g. sodium hydroxide in pellets are placed in a nickel-lined autoclave of about 500 cc. capacity. A mixture of 20 cc. ethanol and 235 cc. ethyl chloride are added. After closing the autoclave, it is fastened in a steel frame revolving in an oil bath so that the autoclave is subjected to a tumbling motion. The stirring effect may be increased by placing a few nickel-lined steel balls in the autoclave. The temperature of the oil bath is constant at 130° C. After five hours' heating, the autoclave is cooled below room temperature and its content is gradually introduced into boiling water. The volatile constituents of the reaction mixture distil off and are recovered by condensation, while the product forms a white, flocculent precipitate. The latter is filtered and washed with water until free from salt. The dry product has an ethoxyl content of about 48%.

Example II

Twenty-eight grams linters which have been conditioned in 100% humidity are treated in a silver-lined autoclave of the same construction and having the same arrangements for heating and agitation as that in Example I, with 54 g. of sodium hydroxide and a mixture of 20 cc. ethanol with 235 cc. ethyl chloride. The temperature is kept constant at 120° C. for about fifteen hours; the autoclave is then cooled and opened and its contents are transferred into a mixer. By the addition of hot water, the excess ethyl chloride and the diethyl ether formed as by-product are expelled and recovered by condensation, while the ethyl cellulose breaks up into small white crumbs, which are washed with hot water to remove the salt. The dry product has an ethoxyl content of 49.3% and its specific viscosity in ½% xylene-butanol solution (80:20 by volume) is 4.31.

Example III

Fifty-two grams purified cotton linters of 7% moisture content are soaked with 500 cc. ethanol, the excess of which is removed by pressing after 12–24 hours. The weight of the alcohol-wet linters is about 84 g.; 104 g. sodium hydroxide and 450 cc. ethyl chloride are added and the whole is treated in a steam-jacketed, Monel metal autoclave equipped with mechanical stirrer. The temperature is kept constant at 120° C., while the stirring is at first, quite slow, and later somewhat faster. After 12–13 hours' treatment, the heating is stopped, the volatiles are distilled off and the residual mass, still hot, is stirred with hot water. The product, ethyl cellulose, breaks up into small crumbs, which are filtered and washed free from salt. The yield is about 69 g., which is almost 100% of the theoretically possible, when the ethyl cellulose, as in this case, contains about 48.5% ethoxyl.

Example IV

Twenty-six grams purified cotton linters, 300 cc. anhydrous ethanol and 60 g. sodium hydroxide in pellets are placed in a bottle and the whole is fastened in a revolving frame so as to effect tumbling motion. After 24–36 hours the sodium hydroxide is dissolved and the linters are pressed to remove the excess alcoholic caustic solution. The residual weight of the moist linters is about 70 g. with a caustic content of about 23 g. Forty-six grams more solid sodium hydroxide and 235 cc. ethyl chloride are added and the whole is treated for 15–16 hours at 110° C. in one of the autoclaves described in the previous examples. The product is then separated from the reaction mixture according to one of the methods described before. It has a specific viscosity of 4.500.

It will be understood that the details and examples hereinbefore set forth are illustrative only, and the invention as herein broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. A process for the preparation of an alkyl ether of cellulose comprising reacting cellulose with an alkylating agent and an alkali, in the presence of a lower monohydric aliphatic alcohol in amount within the range of about 20% to about 90% by weight of the cellulose present.

2. A process for the preparation of an alkyl ether of cellulose comprising reacting cellulose with an alkylating agent and an alkali, in the presence of a lower aliphatic alcohol containing the same alkyl group as contained in the alkylating agent, and in amount within the range of about 20% to about 90% by weight of the cellulose present.

3. A process for producing an alkyl ether of cellulose comprising reacting cellulose with an alkyl halide and an alkali, in the presence of an aliphatic alcohol containing an alkyl group corresponding to the alkyl group contained in the alkyl halide and in amount within the range of about 20% to 90% by weight of the cellulose present.

4. A process for producing an alkyl ether of cellulose comprising reacting cellulose with an alkyl halide and an alkali, in the presence of an aliphatic alcohol containing an alkyl group corresponding to the alkyl group contained in the alkyl halide and in amount within the range of about 40% to 70% by weight of the cellulose present.

5. A process for the preparation of an alkyl ether of cellulose comprising reacting cellulose with an alkylating agent and an alkali, in the

presence of a lower monohydric aliphatic alcohol in amount within the range of about 40% to about 70% by weight of the cellulose present.

6. A process for the production of ethyl cellulose which comprises reacting cellulose with ethylating agent and an alkali, in the presence of ethanol in amount within the range of about 20% to 90% by weight of the cellulose present.

7. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride and an alkali, in the presence of ethanol in amount within the range of about 20% to 90% by weight of the cellulose present.

8. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride and an alkali, in the presence of ethanol in amount within the range of about 40% to 70% by weight of the cellulose present.

9. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride and an alkali, in the presence of ethyl alcohol in amount within the range of about 20% to about 90% by weight of the cellulose present and at a temperature within the range of about 100° C. to about 130° C.

10. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride in the presence of alkali, ethyl alcohol and water, the ethyl alcohol being present in amount within the range of about 20% to about 90% by weight of the cellulose present, and the water being present in amount not in excess of about 100% by weight of the cellulose present.

11. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride in the presence of alkali, ethyl alcohol and water, the ethyl alcohol being present in amount within the range of about 40% to 70% by weight of the cellulose present and the water being present in amount not in excess of about 30% by weight of the cellulose present.

12. A process for the production of ethyl cellulose which comprises reacting cellulose with ethyl chloride in the presence of alkali, ethyl alcohol and water at a temperature within the range of about 100° C. to about 130° C., the ethyl alcohol being present in amount within the range of about 40% to 70% by weight of the cellulose present and the water being present in amount not in excess of about 30% by weight of the cellulose present.

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